

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference D-03007 PCT	FOR FURTHER ACTION		See Form PCT/PEA/416
International application No. PCT/EP2004/013107	International filing date (day/month/year) 18.11.2004	Priority date (day/month/year) 18.11.2003	
International Patent Classification (IPC) or national classification and IPC C07C303/32, C07C67/03, C07C69/68, C07C69/70, C07C69/704			
Applicant SASOL GERMANY GMBH			
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 8 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau) a total of 6 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>			
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input checked="" type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>			
Date of submission of the demand 15.09.2005		Date of completion of this report 06.02.2006	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized Officer: Österle, C Telephone No. +49 89 2399-8120 	

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Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
 - ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
 - ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-3, 5, 7-15	as originally filed
4, 6	filed with telefax on 14.11.2005

Claims, Numbers

1-23	filed with telefax on 14.11.2005
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- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
 - ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
 - ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

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Box No. IV Lack of unity of invention

1. ☒ In response to the invitation to restrict or pay additional fees, the applicant has:
- ☐ restricted the claims.
 - ☐ paid additional fees.
 - ☒ paid additional fees under protest.
 - ☐ neither restricted nor paid additional fees.
2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is
- ☐ complied with.
 - ☒ not complied with for the following reasons:
see separate sheet
4. Consequently, this report has been established in respect of the following parts of the international application:
- ☒ all parts.
 - ☐ the parts relating to claims Nos. .

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-23
	No: Claims	
Inventive step (IS)	Yes: Claims	1-6
	No: Claims	6-23
Industrial applicability (IA)	Yes: Claims	1-23
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item IV

Lack of unity of invention

This Authority considers that there are 2 inventions covered by the claims indicated as follows:

- I: Claims 1-5 directed to the production of metal salts of trifluoromethane sulphonic acid
- II: Claims 6-23 directed to the use of metal salts of trifluoromethane sulphonic acid as transesterification catalyst

The reasons for which the inventions are not so linked as to form a single general inventive concept, as required by Rule 13.1 PCT, are as follows:

The technical feature linking the two groups of claims are the metal salts of trifluoromethane sulphonic acid. These salts however are not novel (see Item V below).

In conclusion, the groups of claims are not linked by common or corresponding special technical features and define 2 different inventions not linked by a single general inventive concept.

The application, hence does not meet the requirements of unity of invention as defined in Rules 13.1 and 13.2 PCT.

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

- D1: SCHMEISSER M ET AL: "ZUR CHEMIE DER PERFLUORALKANSULFONSAEUREN" CHEMISCHE BERICHTE, VERLAG CHEMIE GMBH. WEINHEIM, DE, vol. 103, 1970, pages 868-879, XP002019848 ISSN: 0009-2940
- D2: US-A-4 219 540 (JASS, HERMAN E ET AL) 26 August 1980 (1980-08-26)
- D3: OLAH G A ET AL: "BORON, ALUMINUM, AND GALLIUM

TRIS(TRIFLUOROMETHANESULFONATE) (TRIFLATE): EFFECTIVE NEW FRIEDEL-CRAFTS CATALYSTS" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US, vol. 110, no. 8, 1988, pages 2560-2565, XP001033717 ISSN: 0002-7863

- D4: ATSUSHI KAWADA ET AL: "LANTHANIDE TRIFLUOROMETHANESULFONATES AS REUSABLE CATALYSTS: CATALYTIC FRIEDEL-CRAFTS ACYLATION" JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS, CHEMICAL SOCIETY, LETCHWORTH, GB, vol. 14, 21 July 1993 (1993-07-21), pages 1157-1158, XP000564618 ISSN: 0022-4936
- D5: PATENT ABSTRACTS OF JAPAN vol. 2003, no. 07, 3 July 2003 (2003-07-03) & JP 2003 073330 A (WAKEJIMA IKUKO), 12 March 2003 (2003-03-12)
- D6: ISHIHARA ET AL: "Scandium Trifluoromethanesulfonate as an extremely active lewis acid catalyst in acylation of alcohols with acid anhydrides and mixed anhydrides" JOURNAL OF ORGANIC CHEMISTRY, AMERICAN CHEMICAL SOCIETY, EASTON, US, vol. 61, 1996, pages 4560-4567, XP002313300 ISSN: 0022-3263

1. Novelty (Article 33(2) PCT):

- 1.1 The subject-matter of claim 1 relates to the synthesis of metal salts of trifluoromethane sulphonic acids by reacting trifluoromethane sulphonic acid with a metal alcoholate.

In D1 metal salts of trifluoromethane sulphonic acids are synthesized from trifluoromethane sulphonic acid and metal halides.

In D2 metal salts of trifluoromethane sulphonic acids are synthesized from trifluoromethane sulphonic acid and a metal carbonate or sulfide.

In D3 metal salts of trifluoromethane sulphonic acids are synthesized from trifluoromethane sulphonic acid and metal halides.

In D4 metal salts of trifluoromethane sulphonic acids are synthesized from

trifluoromethane sulphonic acid and the corresponding oxide.

The subject-matter of claims 1-5 therefore can be considered novel.

- 1.2 Claim 6 relates to the use of metal salts of trifluoromethane sulphonic acid exhibiting at least one trifluoromethane sulphonic acid group as esterification catalyst for the production of hydroxycarboxylic acid esters by reacting one or several hydroxycarboxylic acids with one or several alcohols, wherein the metal salts of the trifluoromethane sulphonic acid comprise Mg, Ca, Al, Sn, Ti, Zr, Fe, Cu or Zn as metal.

D5 (see automatic English translation of the patent) discloses the use of

- yttrium and lanthanum salts of trifluoromethane sulphonic acid
- as catalyst

- in the reaction of lactic acid with a C₁-C₄ alcohol

(see examples)

wherein

- a hydrocarbon can be used as an entrainer (see abstract and [0013])
- alcohol can be used in excess of the carboxylic acid, for example in a 2 fold excess (see [0012])

D5 does not disclose the use of metal salts of trifluoromethane sulphonic acid comprising Mg, Ca, Al, Sn, Ti, Zr, Fe, Cu or Zn as metal.

The subject-matter of claims 6-13 then can be considered novel.

- 1.3 Claim 14 relates to the use of metal salts of trifluoromethane sulphonic acid exhibiting at least one trifluoromethane sulphonic acid group as esterification catalyst for the production of hydroxycarboxylic acid esters by transesterification of a hydroxycarboxylic acid ester with at least one hydroxy group and at least one carboxylic acid ester group with an alcohol, or another ester, whereby at least one alcohol is removed from the reaction mixture, wherein the metal salts of the trifluoromethane sulphonic acid comprise Mg, Ca, Al, Sn, Ti, Zr, Fe, Cu or Zn as metal.

D5 does disclose the transesterification of a hydroxycarboxylic acid ester with at least one hydroxy group and at least one carboxylic acid ester group with an alcohol, or another ester (see [0007]-[0008]).

The removal of alcohol during the esterification/transesterification reaction is disclosed in the examples and in [0012].

D5 does not disclose the use of metal salts of trifluoromethane sulphonic acid comprising Mg, Ca, Al, Sn, Ti, Zr, Fe, Cu or Zn as metal.

The subject-matter of claims 14-23 therefore is considered novel.

2. Inventive Step (Article 33(3) PCT):

- 2.1 Claim 1 of the present application differs from D1-D4 in that a metal alcoholate is used to synthesize the desired compounds.

In using an alcoholate as the starting material the product is easily separated from the starting materials and is produced in high yields.

The technical problem in view of D1-D4 then can be seen in providing an alternative method for synthesizing metal salts of trifluoromethane sulphonic acids.

The problem is solved by the process of claim 1. This solution to the technical problem could not be arrived at from D1-D4 or a combination thereof.

The subject-matter of claims 1-5 therefore can also be considered inventive.

- 2.2 Applicant claims that the Mg, Ca, Al, Sn, Ti, Zr, Fe, Cu or Zn metal salts of trifluoromethane sulphonic acids are less prone to hydrolyse than those of Li, Na, K, Ba, In, Sc, Y, La and Ag. Reference was made to D1, p. 871.

D1 does disclose that trifluoromethane sulphonic acid salts of Zr, Th, Ti, Si, Sn and Pb (these are the ones disclosed in D1) are prone to hydrolyse.

There then seems to be a discrepancy between the claim of the Applicant and D1,

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since the Applicant asserts that the salts of Zr and Sn are stable.

In lack of any conclusive data it is at present not possible to determine whether all metal salts of claims 6 and 14 can be used as esterification catalysts.

The subject-matter of claims 6-23 therefore are not considered inventive.

3. Industrial Applicability (Article 33(4) PCT):

The subject-matter of claims 1-23 is considered industrially applicable.

Currently, proton-acidic or Lewis-acidic catalysts are used for the esterification process. These catalysts are frequently protonic acids such as hydrochloric acid, sulphuric acid, phosphoric acid, methane sulphonic acid, *p*-toluene sulphonic acid or acidic ion exchangers. Apart from the protonic acids, which frequently cause problems by corrosion, Lewis acids are also known as esterification catalysts, e.g. using metal halides or strongly acidic styrene resin in combination with the Lewis acid AlCl_3 .

In the case of most esterification processes known from the state of the art, the water formed in the reaction is removed from the reaction mixture by azeotropic distillation by means of an entrainer. For this purpose, aliphatic and aromatic hydrocarbons are usually used.

Surprisingly enough, it has been found that hydroxycarboxylic acid esters can be obtained by the direct esterification of hydroxycarboxylic acids with alcohols in the presence of metal triflate catalysts which, moreover, exhibit an unusually high activity. The reaction times are short even when small quantities of catalysts are used. Depending on the alcohol used, the reaction times are usually 5 to 14 hours.

According to a further embodiment of the invention, the metal triflates, as described above, are used as catalysts for the transesterification of hydroxycarboxylic acid esters.

The metal triflates with at least one trifluoromethane sulphonic acid group are, in this case, brought into contact with hydroxycarboxylic acid esters, preferably with heating, with an alcohol and/or a further hydroxycarboxylic acid ester. As a rule, alcohols are used with a higher boiling point than the alcohol bound in the ester such that the alcohol with a lower boiling point is driven out of the reaction mixture. In this case, ~~Li, Na, K, Ba, Mg, Ca, Al, In, Sn, Se, Y, La, Ti, Zr, Fe, Cu, Ag or Zn,~~ particularly preferably Al, Ti or Zr are preferably used as metal component of the metal triflates.

The alcohols and/or alcoholate groups used for the esterification and transesterification can be branched, straight chain, saturated, unsaturated, aromatic, primary, secondary or tertiary and exhibit preferably 1 to 28 carbon atoms and, if necessary, 1 to 8 ether groups or 1 to 5 further hydroxy groups. The reacted aliphatic

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The metal triflates can be produced in a simple manner as solids or in solution by reacting the acid with a metal alcoholate, as described above. In this respect, it is particularly advantageous that reaction products which have not been purified and contain e.g. suitable alcohols can also be used directly in the esterification reaction.

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However, other processes are also known according to which aluminium salts or rare earth metal salts of trifluoromethane sulphonates are available, e.g. from the corresponding metal carbonates according to US 4,219,540 already cited above.

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The metal triflates have a high Lewis acid activity and are stable in aqueous media. They can therefore be considered for use for numerous organic reactions in which water is contained in the starting materials, is formed as reaction product or used as solvent and/or in micro-emulsions. Thus, the metal triflates according to the invention are generally suitable in particular for reactions in protic media.

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Hydroxycarboxylic acids according to the meaning of this invention are hydroxycarboxylic acids which contain at least one alcohol function (-OH) and one carboxylic acid function (COOH, including COO).

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For the present invention, the following hydroxycarboxylic acids, are suitable in particular as compounds obtained from raw materials both for the esterification reaction and the transesterification reaction: glycolic acid, lactic acid, β -hydroxy propionic acid, α -hydroxybutyric acid, β -hydroxybutyric acid and γ -hydroxybutyric acid, malic acid, tartaric acid, citric acid, mandelic acid and salicylic acid.

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These hydroxycarboxylic acids are reacted with primary, secondary and tertiary, straight chain and branched alcohols with a chain length of 1 of 28 carbon atoms. Metal salts of trifluoromethane sulphonic acid (triflates) are used as catalysts. The following are used as metals: ~~Li, Na, K, Ba~~, Mg, Ca, Al, ~~In~~, Sn, ~~Se~~, ~~Y~~, ~~La~~, Ti, Zr, Fe, Cu, ~~Ag~~ and Zn.

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The hydroxycarboxylic acid esters of the above-mentioned acids have a variety of applications. The esters of lactic acid with ethanol and *n*-butanol (ethyl lactate and *n*-butyl lactate) are used, among other things, as environment-friendly additives in solvent formulations for paints and in purifier formulations for the semiconductor industry. In this case, they are used for removing photo resists from templates, for example. In addition, both esters have been approved by the FDA as additives in the

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17. 11. 2005 - 16 -

CLAIMS

(83)

1. Process for the production of metal salts of trifluoromethane sulphonic acid comprising at least one trifluoromethane sulphonic acid group by reacting
5 trifluoromethane sulphonic acid $\text{CF}_3\text{SO}_3\text{H}$ with a metal alcoholate, optionally in the presence of a solvent, at a temperature of -40°C to $+100^\circ\text{C}$, the metal being Li, Na, K, Ba, Mg, Ca, Al, In, Sn, Sc, Y, La, Ti, Zr, Fe, Cu, Ag or Zn, preferably Al, Ti or Zr and the alcoholate group(s) of the metal alcoholate comprising independent of each other 1 to 28 carbon atoms as well as
10 optionally hydroxy groups ($-\text{OH}$), ether bonds ($\text{C}-\text{O}-\text{C}$) and/or more than one alcoholate bond ($\text{M}-\text{O}-$).
2. Process according to claim 1 characterised in that the metal salt of the trifluoromethane sulphonic acid is
15 $(\text{CF}_3\text{SO}_3)_m \text{M} (\text{OR})_n$
wherein
the sum of $(m+n)$ corresponds to the valency of the metal cation and m is at least 1,
R is a hydrocarbon moiety with 1 to 6 carbon atoms and, optionally ether
20 bonds ($\text{C}-\text{O}-\text{C}$) or
is hydrogen and R can be different for each n and
M is Mg, Ca, Al, ~~Sc~~_i, Sn, La, Ti, Zr, Cu or Zn.
3. Process according to one of the preceding claims characterised in that the
25 solvent is an alcohol, an aliphatic and/or aromatic hydrocarbon, an ether and/or a ketone, with 2 to 32 carbon atoms respectively, or water or their mixtures.
4. Process according to one of the preceding claims characterised in that the
30 trifluoromethane sulphonic acid, optionally diluted with a solvent, is added to the metal alcoholate, optionally diluted with a solvent.
5. Process according to at least one of claims 1 to 3 characterised in that the
35 metal alcoholate, optionally diluted with a solvent, is added to the trifluoromethane sulphonic acid, optionally diluted with a solvent.

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- 5 6. Use of metal salts of trifluoromethane sulphonic acid exhibiting at least one trifluoromethane sulphonic acid group as esterification catalyst for the production of hydroxycarboxylic acid esters by reacting one or several hydroxycarboxylic acids with one or several alcohols wherein the metal salts of the trifluoromethane sulphonic acid comprise Mg, Ca, Al, Sn, Ti, Zr, Fe, Cu or Zn as metal.
- 10 7. Use according to claim 6 characterised in that the metal salts of the trifluoromethane sulphonic acid comprise ~~Li, Na, K, Ba, Mg, Ca, Al, In, Sn, Se, Y, La, Ti, Zr, Fe, Cu, Ag or Zn as metal,~~ preferably Mg, Zn, Al, Ti or Zr as metal.
- 15 8. Use according to at least one of claims 6 or 7 characterised in that the alcohols exhibit 1 to 28 carbon atoms and, optionally furthermore 1 to 8 ether groups and/or further 1 to 5 hydroxy groups.
- 20 9. Use according to one of claims 6 to 8 characterised in that the esterification is carried out at temperatures of 60 to 250 °C and, independently thereof, at pressures of 0.2 to 10 bar.
- 25 10. Use according to at least one of claims 6 to 9 characterised in that the esterification is carried out in the presence of an entrainer and water is removed by azeotropic distillation, the entrainer being preferably an aliphatic hydrocarbon, an aromatic hydrocarbon, a dialkyl ether or an alcohol, preferably the alcohol used for the esterification itself and/or its/their mixture.
- 30 11. Use according to at least one of claims 6 to 10 characterised in that the molar ratio of the alcohol used to the carbonyl groups of the hydroxycarboxylic acid used is from 1 : 0.5 to 4.0, preferably 1.0 to 2.0.
12. Use according to at least one of claims 6 to 11 characterised in that the catalyst is used in a quantity of 0.05 to 1.0 % by weight, based on the hydroxycarboxylic acid used.
- 35 13. Use according to at least one of claims 6 to 12 characterised in that the esterification is terminated by treating the crude product with metal

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alcoholates, alkali hydroxides or alkaline earth hydroxides and subsequently worked up by distillation.

- 5 14. Use of metal salts of trifluoromethane sulphonic acid exhibiting at least one trifluoromethane sulphonic acid group as a transesterification catalyst for the production of hydroxycarboxylic acid esters by transesterification of a hydroxycarboxylic acid ester with at least one hydroxy group and at least one carboxylic acid ester group (-COO-), optionally having free carboxylic acid groups,
- 10 with an alcohol and/or another ester, whereby at least one alcohol is removed from the reaction mixture, wherein the metal salts of the trifluoromethane sulphonic acid comprise Mg, Ca, Al, Sn, Ti, Zr, Fe, Cu or Zn as metal
- 15 15. Use according to claim 14 characterised in that the metal salts of trifluoromethane sulphonic acid exhibit ~~Li, Na, K, Ba, Mg, Ca, Al, In, Sn, Se, Y, La, Ti, Zr, Fe, Cu, Ag or Zn as metal,~~ preferably Mg, Zn, Al, Ti or Zr as metal.
- 20 16. Use according to at least one of claims 14 or 15 characterised in that the alcohols used comprise 1 to 28 carbon atoms and, optionally 1 to 8 ether groups and/or further 1 to 5 hydroxy groups.
- 25 17. Use according to one of claims 14 to 16 characterised in that the transesterification is carried out at temperatures of 60 to 250 °C and, independently thereof, at pressures of 0.05 to 10 bar.
- 30 18. Use according to at least one of claims 14 to 17 characterised in that the molar ratio of the alcohol employed relative to the ester groups of the hydroxycarboxylic acid ester to be converted is from 0.5 to 2.0.
- 35 19. Use according to one of claims 14 to 18 characterised in that the catalyst is used in a quantity of 0.02 to 1.0 % by weight, based on the hydroxycarboxylic acid ester to be converted.
20. Use according to one of claims 6 to 19 characterised in that the work-up of the hydroxycarboxylic acid ester takes place by distillation at temperatures in the

range of 60 °C to 250 °C and pressures of 1 hPa to 1013 hPa or by stripping with a water vapour steam at temperatures of 120 °C to 200 °C and pressures of 1 hPa to 1013 hPa, in particular directly from the crude product or after removal of the catalyst and filtration of the crude product.

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21. Use according to claim 20 characterised in that the distillative work-up takes place after prior removal of the catalyst with activated carbon, aluminium hydroxide or aluminosilicate.

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22. Use according to any of claims 6 to 21 wherein the metal salts of trifluoromethane sulphonic acid are used in the presence of water.

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23. Use according to claim 22 wherein the metal salts of trifluoromethane sulphonic acid are used in an aqueous environment comprising water, in particular as solvent or diluent, in addition to any water being formed in the course of the reaction.

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